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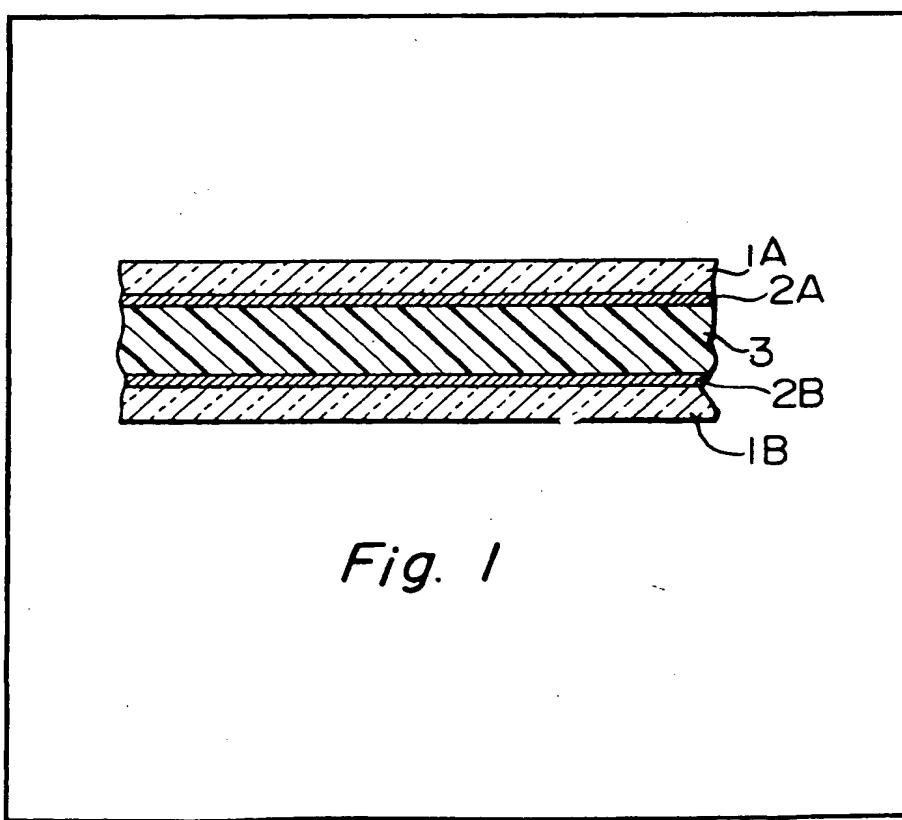
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(54) Laminated panel

(57) A laminated panel composed of a plastics sheet 3 and a glass sheet 1A, 1B bonded to each other through an adhesive layer 2B, 2C having a thickness of less than 200 microns and composed of a thermoplastic resin having a softening point of less than 100°C, containing substantially no plasticizer and being plastic at room temperature, said plastics sheet being composed of a resin having a higher softening point than said thermoplastic resin.



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Fig. 5-a

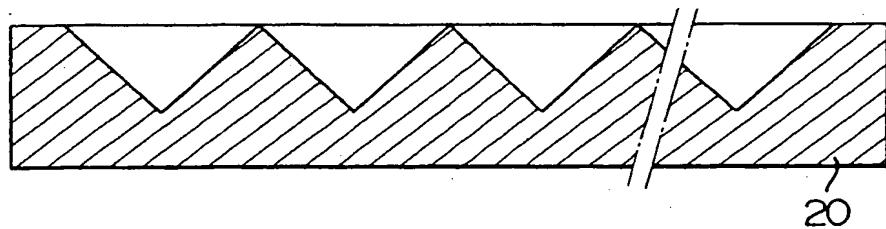


Fig. 5-b

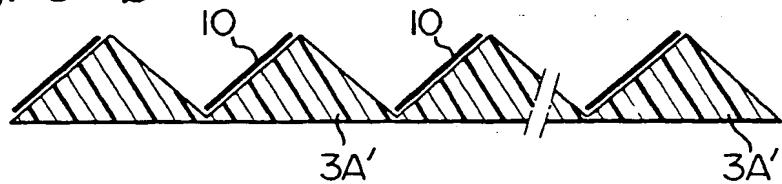


Fig. 5-c

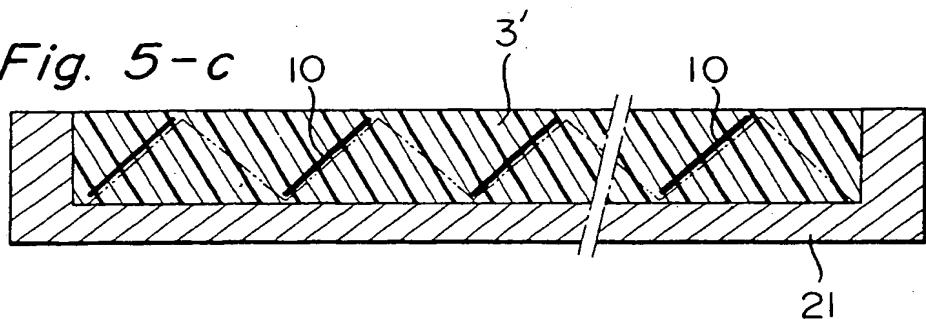
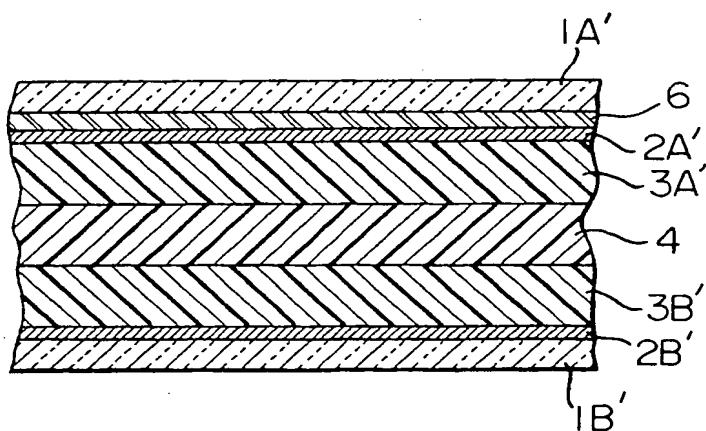


Fig. 6



In accordance with this invention, the objects and advantages of this invention are achieved by a laminated panel comprising a plastic sheet and a glass sheet bonded to each other through an adhesive layer having a thickness of less than about 200 microns and composed of a thermoplastic resin having a softening point of less than about 100°C, containing substantially no plasticizer and being plastic at room temperature, said plastic sheet being composed of a resin having a higher softening point than said thermoplastic resin.

These objects and advantages of this invention, according to another aspect, are achieved by a laminated panel comprising a glass sheet forming an outermost layer, an adhesive layer having a thickness of not more than about 200 microns and composed of a thermoplastic resin having a softening point of less than about 100°C, containing substantially no plasticizer and being plastic at room temperature, a first plastic sheet, a cushioning layer and a second plastic sheet, said glass sheet being bonded to one surface of said first plastic sheet through said adhesive layer, and the other surface of said first plastic sheet being bonded to one surface of said second plastic sheet through said cushioning layer.

One characteristic feature of the laminated panel of this invention is that the adhesive layer is composed of a thermoplastic resin which has a softening point of less than about 100°C, is substantially free from a plasticizer and is plastic at room temperature, and it has a thickness of less than about 200 microns.

Since the thermoplastic resin as the adhesive layer between the glass sheet and the plastic sheet shows plasticity at room temperature, it reduces external shock under service conditions. Furthermore, since this thermoplastic resin has a relatively low softening point of less than about 100°C, it is not necessary to provide too large a temperature difference between the heat-sealing temperature which is higher than the softening point of the thermoplastic resin and the room temperature at which cooling subsequent to heat sealing is performed. The adhesive layer has plasticity at room temperature and the action of thermal stress causes it to show a plastic flow. Consequently, the strain attributed to the difference in the coefficient of thermal expansion between the glass sheet and the plastic sheet can be minimized, and a laminated panel free from a mechanical strain, an optical strain, deformation and cracks can be obtained. Moreover, since the thermoplastic resin does not contain a plasticizer, haze of the plastic sheet owing to the migration of plasticizer from the adhesive layer to the plastic sheet does not occur at the time of heat sealing, and therefore, a laminated panel having good transparency can be obtained.

It can be anticipated to some extent that the

thermoplastic resin having plasticity at room temperature used in the adhesive layer would be able to reduce external shock in use at room temperature by its own plastic deformation. Investigations of the present inventors have shown that by adjusting the thickness of the adhesive layer to less than about 200 microns, preferably about 40 to about 100 microns, the plastic deformation which may be generated at the time of reducing external shock scarcely remains in the adhesive layer, and therefore, a laminated panel can be provided which does not have a mechanical strain or optical distortion and is free from deformation or cracking even after it has undergone shock.

Preferably, the thermoplastic resin having a softening point of less than about 100°C and plasticity at room temperature as the adhesive layer in this invention is selected from vinyl acetate homopolymer, isobutylene homopolymer, and copolymers of vinyl acetate or isobutylene with other copolymerizable ethylenic monomers. These resins are used in a substantially plasticizer-free form.

Examples of the copolymers of vinyl acetate or isobutylene and other copolymerizable ethylenic monomers include copolymers of vinyl acetate or isobutylene with ethylene, propylene, styrene, α -methylstyrene, acrylic acid, methacrylic acid, acrylates such as methyl acrylate or ethyl acrylate, methacrylates such as methyl methacrylate or ethyl methacrylate.

Copolymers of vinyl acetate and ethylene and/or acrylic monomers are preferred, and a copolymer of ethylene and vinyl acetate is especially preferred.

The proportion of units derived from vinyl acetate or isobutylene in the copolymer is desirably about 17 to about 57 mole%, especially about 24 to about 44 mole%, based on the sum of the units derived from vinyl acetate or isobutylene and units derived from the copolymerizable ethylenic monomer.

Of the polymers exemplified hereinabove, polyvinyl acetate, polyisobutylene, and copolymers containing about 17 to 57 mole% of units derived from vinyl acetate are preferred as the adhesive layer.

A vinyl acetate/ethylene copolymer composed of about 17 to about 57 mole%, above all about 24 to about 44 mole%, of units derived from vinyl acetate and about 83 to about 43 mole%, above all about 76 to about 56 mole% of units derived from ethylene is especially advantageous because it has the properties required in this invention and shows plasticity, but does not show crystallinity, at lower temperatures, for example at temperatures of - 20°C.

Another characteristic feature of the thermoplastic resin used in this invention is that a plastic flow is caused in the adhesive layer under a lower stress than that on adhesive layers in conventional laminated panels, which

tetramethylene glycol and polyesters such as adipic esters as a polyol component and aliphatic or alicyclic isocyanates such as hexamethylene diisocyanate or its derivatives or aromatic isocyanates such as 2,4-/2,6-toluene diisocyanate or 1,5-naphthalene diisocyanate as an isocyanate component. Those prepared by using aliphatic or alicyclic polyisocyanates as the isocyanate component are preferred

5 because their yellowing with time is reduced.
The polyvinyl butyral resin is, for example, the one containing 15 to 20% by weight of hydroxyl groups and 0 to 4% by weight of acetate groups and the remainder being butyral groups, and contains as a plasticizer 20 to 45 parts, per 100 parts by weight of the resin, triethylene glycol di-2-ethyl butyrate or dibutyl sebacate or dihexyl adipate or dioctyl adipate.

20 A preferred species of the ethylene/glyl acetate copolymer is the one containing about 17 to about 57 mole%, based on the entire structural units, of units derived from vinyl acetate already exemplified hereinabove as the thermoplastic resin for forming the adhesive layer.

25 As can be appreciated from the foregoing description, the laminated panel of this invention including a cushioning layer is characterized by having such a structure that a shock exerted externally is absorbed by the cushioning layer. Accordingly, most basically, this laminated panel consists of a glass sheet 1A' forming an outermost layer, an adjacent layer 35 2A', an adjacent plastic sheet 3A', an adjacent cushioning layer 4 and an adjacent plastic sheet 3B' forming another outermost layer.

30 A further developed embodiment of the laminated panel of this invention having a cushioning layer is shown in Fig. 3.

In Fig. 3, the reference numerals 1A'' and 1B'' represent a glass sheet; 2A'' and 2B'', adhesive layers; 3A'' and 3B'', plastic sheets, 4A'' and 4B'', cushioning layers; and 5, 45 another sheet-like material.

The embodiment shown in Fig. 3 differs from that shown in Fig. 2 in that it further has the other sheet 5 (therefore, two cushioning layers are used). The plastic sheet, the glass sheet, the adhesive layer and the cushioning layer are as already described. The laminated panel in accordance with this embodiment having the other sheetlike material has high penetration resistance to shock exerted externally, and therefore bullet penetration resistance can be easily imparted. Even a mechanically weak sheet-like material can be made into a laminated panel having practical strength because it is protected on both sides 55 with cushioning layers, plastic sheets and glass sheets.

60 As the other sheet-like material, there can be used not only plastic sheets of the same materials as the aforesaid plastic sheets. Other plastic sheets, glass sheets, and metal sheets

can also be used.

65 The laminated panel shown in Fig. 3 having the same structure on both sides of the other sheet-like material resists shock in the same way whichever outermost layer is subject to shock. A laminated panel having a cushioning layer, one outermost layer of which consists of a plastic sheet, resists shock in the same way as in the embodiment shown in Fig. 3 only 70 when the shock is inserted on the surface of the glass sheet forming the other outermost layer.

75 The individual members of the laminated panel of this invention, i.e. the glass sheet, 80 plastic sheet, adhesive layer, and optionally cushioning layer and other sheet-like material, can be used either as colored or non-colored transparent members, or as colored or non-colored non-transparent members. Preferably, 85 these members are transparent, and by using these transparencies members, a transparent laminated panel can be provided.

90 The laminated panel of this invention can be produced by providing an adhesive layer 95 having a thickness of less than about 200 microns composed of a thermoplastic resin having a softening point of not more than about 100°C and being substantially free of a plasticizer and being plastic at room temperature on the surface of either one of a glass sheet and a plastic sheet to be bonded, or filling the aforesaid adhesive into a space between a glass sheet and a plastic sheet located a predetermined distance from each 100 other, then maintaining the assembly at a temperature higher than the softening point of the thermoplastic resin, usually at a temperature about 1 to about 30°C higher than the softening point, and a pressure of 1 to 15 kg/cm² for a period of about 1 to about 30 minutes, and cooling the product to room temperature under pressure, or after or while releasing the pressure.

105 110 The adhesive layer can be provided, for example, by coating the adhesive. When the adhesive is solid at room temperature, it may be provided by using a film of the adhesive molded to the desired thickness.

115 The laminated panel of this invention having a cushioning layer can be produced by making a material composed of a bonded structure of glass sheet/adhesive layer/plastic sheet in the above manner, and bonding it to a cushioning layer; or first making a material 120 composed of a plastic sheet/cushioning layer/plastic sheet and bonding it to a glass sheet by an adhesive as described above; or bonding a glass sheet, and a plastic sheet by means of an adhesive and a cushioning layer.

125 130 Bonding by a cushioning layer can be achieved without the aid of another adhesive when the highly elastic resin forming the cushioning layer is adhesive to the plastic sheet. If the highly elastic resin forming the cushioning layer is non-tacky or non-adhesive,

3B' or the cushioning layer 4. In the embodiment of Fig. 3, such films or fabrics can be embedded in any one of the plastic sheet 3A'' or 3B'', the cushioning layer 4A'' or 4B'' or the other sheet-like material (in this case, limited to a plastic sheet-like material).

5 Examples of the films having light-shielding function include films of metals such as aluminum, palladium, gold, silver, copper, iron, 10 nickel, chromium, lead or tin, films of metal alloys, films of metal oxides such as indium oxide or tin oxide, colored nontransparent plastic films colored by organic or inorganic pigments, thin films of wood, and paper 15 sheets.

Instead of the films having light-shielding ability, woven or knitted fabrics may be used. Examples are woven or knitted fabrics of polyester fibers, polyamide fibers, polypropylene fibers, acrylic fibers, cellulose acetate fibers, glass fibers, carbon fibers, cotton, and wool. Preferably, the mesh openings of these woven or knitted fabrics are dense to such an extent that the desired light-shielding function 25 is imparted.

When the films or knitted or woven fabrics having light-shielding function are composed of a material having electric conductivity, such as metal films or woven or knitted fabrics of 30 carbon fibers, an electric current may be passed through them. Heat generation by passing current prevents clouding of the surface of glass by dew formation.

35 Figs. 5-a, 5-b and 5-c are cross-sectional views showing the process for embedding films or knitted or woven fabrics having light-shielding ability in a plastic sheet.

Fig. 5-a shows a mold 20 having a sawtooth-like cross section. A resin for forming the plastic sheet 3' (see Fig. 4) in accordance with this invention is poured into the mold 20. When the resin is a thermoplastic resin, it is then cooled and solidified. When it is a thermosetting resin, it is heated and 45 solidified, followed by cooling. Thus, the sawtooth-like sheet 3'A in Fig. 5-b is produced. Then, as shown in Fig. 5-b, films or woven or knitted fabrics 10 having light-shielding ability are bonded to the same side 50 surfaces of the sawteeth of the sawtooth-like sheet 3A'. The resulting assembly is placed in a recessed plate-like mold 21 shown in Fig. 5-c, and a resin (usually the same type of resin as used to form the sawtooth-like sheet 3'A) is 55 poured into the mold 21 and solidified or cured in the same way as above. Thus, a sheet having films or fabrics having light-shielding function embedded therein can be produced.

60 Fig. 6 is a longitudinal sectional view of one embodiment of the laminated panel having the ability to reflect heat rays. In Fig. 6, the reference numerals 1A' and 1B' represent glass sheets; 2A' and 2B', adhesive layers; 65 3A' and 3B', plastic sheets, 4, a cushioning

layer; and 6, a layer having the ability to reflect heat rays.

The embodiment shown in Fig. 6 corresponds to the embodiment shown in Fig. 2. It will be appreciated that a laminated panel having the ability to reflect heat rays is present also with respect to the embodiments shown in Figs. 1 and 3. In Fig. 6, the layer having the ability to reflect heat rays is located adjacent to the glass sheet 1A'. But its position is not limited to it. For example, it may be located adjacent to the glass sheet 1B'. Or it may be located adjacent to that surface of the plastic sheet 3A' or 3B' which faces the cushioning layer 4', or that surface of the plastic sheet 3A' or 3B' which faces the adhesive layer 2A' or 2B'.

A film having the ability to reflect heat rays can be provided adjacent to the plastic sheet 85 3 or to that surface of the glass sheet 1A or 1B which faces the adhesive layer in the embodiment of Fig. 1. In the embodiment of Fig. 3, it may be provided adjacent to that surface of the glass sheet 1A'' or 1B'' which 90 faces the adhesive layer, or to that surface of the plastic sheet 3A'' or 3B'' which faces the adhesive layer, or to that surface of the plastic sheet 3A'' or 3B'' or the other sheet-like material 5 which faces the cushioning layer.

95 The layer having the ability to reflect heat rays can be provided, for example, by depositing a metal in thin film (e.g., about 20 to about 3000 Å thick) on a glass sheet by a chemical means such as plating, or depositing 100 a metal in thin film on the glass sheet by physical means such as vacuum deposition. By using such a glass sheet in such a way that its metal-deposited surface faces inward, a laminated panel of the structure shown in 105 Fig. 6 can be provided by the present invention.

The layer having the ability to reflect heat rays may be a plastic film having a metal 110 vacuum-deposited thereon. Such a plastic film having the ability to reflect heat rays is readily available commercially. For example, a polyester film having aluminum metal vacuum-deposited thereon can be used.

In the production of the laminated panel of 115 this invention using such a plastic film having the ability to reflect heat rays, the heat ray-reflecting film may be bonded to a glass sheet or plastic sheet by using a known adhesive or the resin forming the adhesive layer used in 120 this invention.

As can be seen from the foregoing description, the present invention can also provide a laminated panel having films or woven or knitted fabrics having light-shielding ability 125 and a layer having the ability to reflect heat rays.

The light-shielding laminated panel in accordance with this invention is used suitably as windowpanes of vehicles and buildings which 130 require light shielding, or as outdoor display

This laminated panel showed a good light-shielding effect. When the laminated panel was placed horizontal on a wooden frame, and a steel ball weighing 225g was let fall onto the plane from a height of 2.5 m. No breakage was seen on the outermost glass sheets. Thus, it was ascertained that this laminated panel had higher break strength than a commercially available laminated glass composed of two glass sheets having a thickness of 2.3 mm bonded to each other through an interlayer of resin.

Example 4

15 Aluminum was vacuum-deposited on one surface of a glass sheet having a size of 300 mm × 300 mm × 1.0 mm, and a toluene solution of the same vinyl acetate/ethylene copolymer as used in Example 1 was coated on 20 the aluminum-deposited surface of the glass sheet using a spray gun to form a coated film having a thickness of about 0.06 mm.

The same polycarbonate sheet having an interlayer of silicone resin as produced in 25 Example 2 was superimposed on the coated surface of the glass sheet. The assembly was pressed by a roll at a temperature of about 100°C, and then treated in an autoclave at 120°C and 13 kg/cm²·G for 30 minutes, 30 and then cooled to room temperature.

The resulting laminated panel exhibited moderate light-transmitting property and high reflection of heat rays, and showed impact strength, equal to, or higher than, a laminated 35 glass composed of two glass sheets having a thickness of 5 mm.

Example 5

40 A polyethylene terephthalate film having aluminum vacuum-deposited thereon was bonded to one surface of a glass sheet having a size of 300 mm × 300 mm × 0.6 mm using an acrylic emulsion adhesive (70% by weight of 45 2-ethylhexyl acrylate, 29% by weight of vinyl acetate and 1% by weight of acrylic acid).

Separately, a polyurethane resin (composed mainly of 100 parts by weight of polyester-polyol and 8 to 10 parts by weight of 50 2,4/2,6-toluene diisocyanate; "POLYLITE OD-X106", a product of Dainippon Ink and Chemical Inc.) was poured into the space between two polycarbonate resin sheets having a size of 300 mm × 300 mm × 2 mm, 55 and heated at 100°C for 1 hour to form a polycarbonate laminated sheet having an interlayer of polyurethane (thickness 2 mm).

An adhesive resin composed of an ethylene/vinyl acetate copolymer (composed 45% by weight of ethylene and 55% by weight of 60 vinyl acetate) was coated to a thickness of 0.06 mm on the aluminum-deposited surface of the glass sheet.

The polycarbonate sheet was sandwiched 65 between two such glass sheets, and the as-

sembly was heated to 100°C and roll pressed by a roll, and further heat-treated at 110°C for 30 minutes at a pressure of 10 kg/cm²·G. Then, the laminate was cooled to about 40°C, and the pressure was reduced.

The resulting laminated panel had an equivalent heat ray reflectance to commercially available highly heat ray reflective glasses, and showed an impact strength equal to, or 75 greater than, a laminated glass obtained by bonding glass sheets having a thickness of 5 mm.

CLAIM

80 1. A laminated panel composed of a plastics sheet and a glass sheet bonded to each other through an adhesive layer having a thickness of less than 200 microns and composed of a thermoplastic resin having a softening point of less than 100°C, containing substantially no plasticizer and being plastic at room temperature, said plastics sheet being composed of a resin having a higher softening point than said thermoplastic resin.

85 2. A laminated panel according to claim 1 wherein said thermoplastic resin forming said adhesive layer is selected from vinyl acetate homopolymer, isobutylene homopolymer and copolymers of vinyl acetate or isobutylene 95 with at least one other copolymerizable ethylenic monomer.

90 3. A laminated panel according to claim 2 wherein said thermoplastic resin is a copolymer of vinyl acetate containing not more than 57 mole%, based on the entire structural units, of units derived from vinyl acetate.

95 4. A laminated panel according to claim 3 wherein said copolymer of vinyl acetate contains 1.7 to 44 mole%, based on the total 100 structural units, of units derived from vinyl acetate.

105 5. A laminated panel according to claim 2, 3 or 4 wherein said thermoplastic resin is a copolymer of ethylene, and/or an acrylic 110 monomer, and vinyl acetate.

115 6. A laminated panel according to any one of the preceding claims wherein said adhesive layer is 40 to 100 microns thick.

7. A laminated panel according to any one 120 of the preceding claims wherein said plastics sheet is composed of a polycarbonate resin, acrylic resin, vinyl chloride resin or styrene resin.

8. A laminated panel according to any one 125 of the preceding claims wherein said plastic sheets is 0.5 to 6 mm. thick.

9. A laminated panel according to any one of the preceding claims wherein two glass sheets each forming an outermost layer are 130 each bonded to the opposite surfaces of said plastics sheets through a said adhesive layer.

10. A laminated panel comprising a glass sheet forming an outermost layer, an adhesive layer having a thickness of not more than 200 microns and composed of a thermoplastic